Calcium fluoride nanostructures on Si（001）: surface X-ray diffraction studies

N. Sokolov[1,*], S. Suturin[1], A. Banshchikov[1], R. Kyutt[1], Y. Takeda[2], M. Tabuchi[2], O. Sakata[3], T. Shimura[4], K. Kawamura[4], M. Asakawa[4], and J. Harada[2,5]

[1] Ioffe Institute, St. Petersburg, Russia, [2] Nagoya University, [3] JASRI/SPring-8, [4] Osaka University, [5] Rigaku Co.

In this work, surface X-ray diffraction （SXRD） is applied to study the structure of the fluoride wetting layer forming during CaF_2 deposition onto Si （001） surface kept at 750℃. Samples with three different coverages of 0.7, 1.0 and 2.0 monolayer were grown and in-situ characterized by SXRD to reveal 3 × 1-like surface reconstruction consistent with previous studies by electron diffraction. A number of unknown before features in diffraction intensity profiles have been found. The analysis of the collected structural data is underway.

The growth of CaF_2 on Si（111） has been the object of intense investigations in recent years [1], however only few attempts were done to study CaF_2 on technologically important Si（001）[2, 3]. As it was shown recently[4], exposure of the heated to 650-750℃ Si（001） surface to CaF_2 molecular beam results in formation of strongly anisotropic calcium silicide wetting layer. During this process, transformation from initial two domain （2 × 1 + 1 × 2） Si（001） surface to 3 × 1 reconstructed single domain surface of the wetting layer takes place. It was found that the wetting layer determines further nucleation and growth of CaF_2 stripes （typical dimensions: few nanometer in height and width, microns in length） that exhibit unusual CaF_2 （110） /Si（001） epitaxial relations. At higher coverage, the fluorite stripes coalesce forming CaF_2 （110） layer with a nanometer scale grooved and ridged surface, which can be used as a chemically inert highly anisotropic template for fabrication of quasi-one dimensional nanostructures. Moreover, CaF_2 stripes forming on the wetting layer could be attractive as insulating lines or for nano-lithographic purposes.

It is expected that the experiments at BL13XU beamline aiming at determination of the atomic structure of the wetting layer and the entire CaF_2 （110）/Si（001） interface will considerably contribute to deeper understanding the processes taking place during its formation. Furthermore, it has been recently found that the wetting layer can be used as passivating crystalline film for formation on Si（001） magnetic nanostructures attractive for applications in spintronics [5].

In this experiment, surface X-ray diffraction （SXRD） was applied to investigate CaF_2

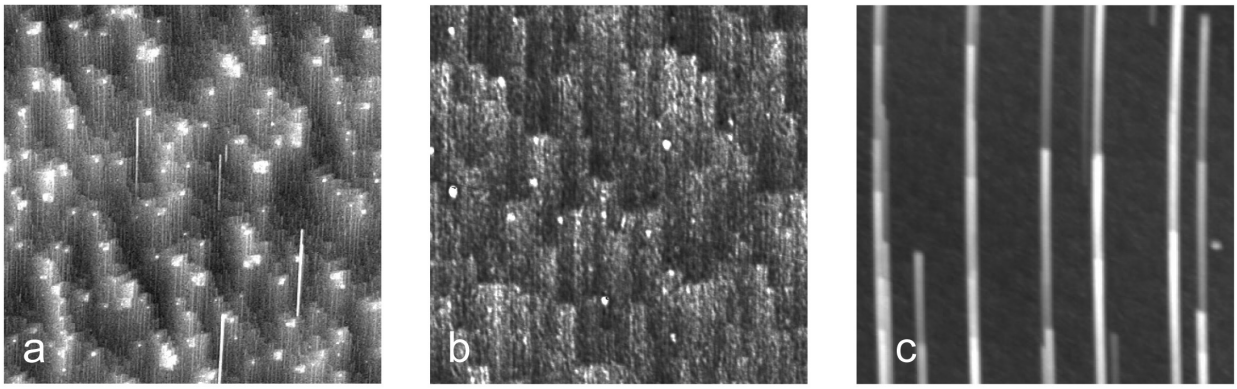

Fig. 1 AFM images of CaF_2 / Si(001)samples: 0.7 ML(a), 1.0 ML(b), 2.0 ML(c). Image sizes: (a)0.7 × 0.7 μm; (b,c) 2 × 2 μm.

nanostructure formation at the initial stages of growth and to determine the atomic structure of the CaF_2 /Si(001) interface. The samples to be investigated have been grown in situ by molecular beam epitaxy using ultra high vacuum (UHV) preparation chamber installed in the experimental hutch 3 of BL13XU beam line. Prior to the growth Si(001) substrates have been chemically and thermally cleaned to get clean Si surface.

Three samples were grown by depositing 0.7, 1.0 and 2.0 monolayers (ML) of CaF_2 respectively onto Si(001) substrate kept at 750 ℃. The deposition rate measured by Inficon quartz microbalance was ~ 40 sec per ML. The substrate temperature was monitored using an optical pyrometer. The surface structure was monitored in situ by reflection high energy electron diffraction (RHEED). The surface topography of the grown samples was measured afterwards by ambient air atomic force microscopy (AFM). The AFM data (Fig. 1) in combination with RHEED patterns (Fig. 2) appear to be very typical of the CaF_2 growth on Si(001).

The initial Si surface shows clear 2 × 1 + 1 × 2 double domain superstructure characteristic of the clean Si(001) surface (Fig. 2a). The deposition of 0.7 ML of CaF_2 onto this surface at 750 ℃ results in formation of narrow fluorite nanostripes on top of Si terraces (Fig. 1a). The nanostripes are all aligned along Si[1-10] direction thus inducing single domain anisotropy on the surface.

RHEED patterns taken with electron beam

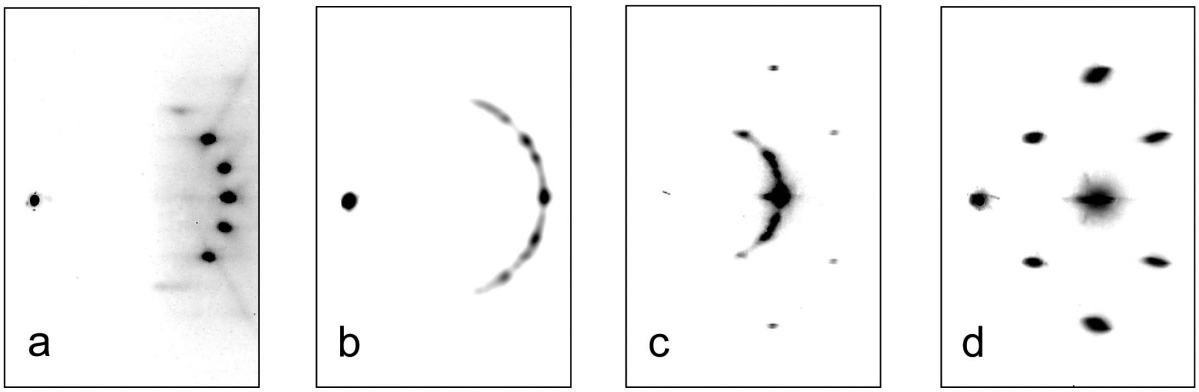

Fig. 2 Typical RHEED patterns of CaF_2 / Si(001)samples. 2 × 1 reconstruction of clean Si surface (a); 3 × 1 reconstruction of the wetting layer (b); ridges on the wetting layer with electron beam parallel (c) and perpendicular (d) to the ridges.

parallel to Si[1-10] show a 3 × 1-like superstructure with periodicity of 3 across the nanostripes (Fig. 2b). The situation is almost the same for the 1.0 ML sample except that the surface is completely covered by the nanostripes forming the wetting layer (Fig. 1b). At higher coverage 3D CaF_2 ridges are nucleated on top of the wetting layer propagating along Si[1-10] direction (Fig. 1c). This is consistent with the highly anisotropic RHEED patterns: with electron beam along the ridges, the 3 × 1 surface reconstruction can be recognized, while with electron beam perpendicular to the ridges, distinct transmission spots appear in the pattern, indicating that CaF_2 lattice in the ridges is oriented with CaF_2 [110] axis normal to Si(001) surface.

For each of the three grown samples a comprehensive SXRD study was carried out using synchrotron radiation with photon energy of 11 keV. The advantage of the UHV chamber mounted on the diffractometer was utilized in the way that after the sample was grown and during the SXRD measurements the sample was always kept in UHV conditions. At the first stage the studies were carried out in the in-plane geometry at L=0.1 and at constant incident angle α =0.6 deg. Surface diffraction profiles were measured along K and H in-plane directions in order to get an overview of the surface reconstruction.

At every intensive reflection an ω-scan was carried out in order to get the integrated intensity. The profiles were mainly taken along K at integer H, that is, perpendicular to the fluoride nanostripes at the surface (Fig. 3). For all the samples the profiles showed strong fractional and

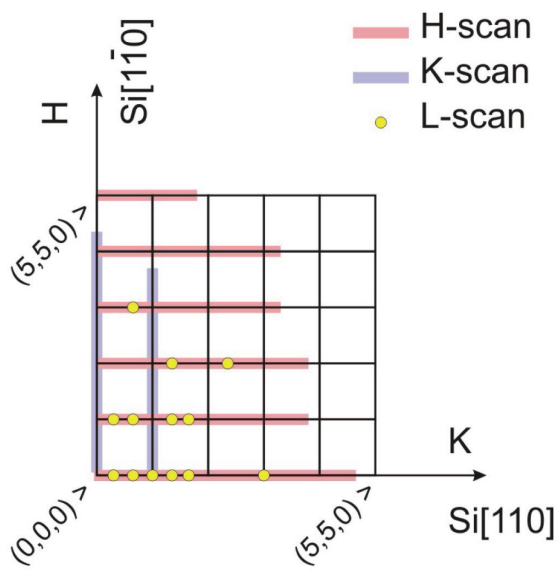

Fig. 3 Map of the carried out SXRD measurements

integer order reflections some of which can be readily identified as belonging to the wetting layer, silicon substrate and CaF_2 ridges respectively (Fig. 4).

On examining the profiles one can notice that all the most intensive fractional order reflections are located in the vicinity of K=N/3 which is consistent with the RHEED patterns showing the 3 × 1 reconstruction. At the first glance, the profiles exhibit an envelop function with maximums at N/3 that is modulated by high frequency oscillation corresponding to the real space periodicity of 16-18. From this one can conclude that the wetting layer can be characterized by an overall periodicity of 3, however there might be some degree of superimposed disorder having a long range periodicity of 16-18. This kind of profile behavior is found to be stable from sample to sample and appears at all three different coverages. It is also noteworthy that for the 2.0 ML coverage the CaF_2 (400) bulk reflection is identified, giving just

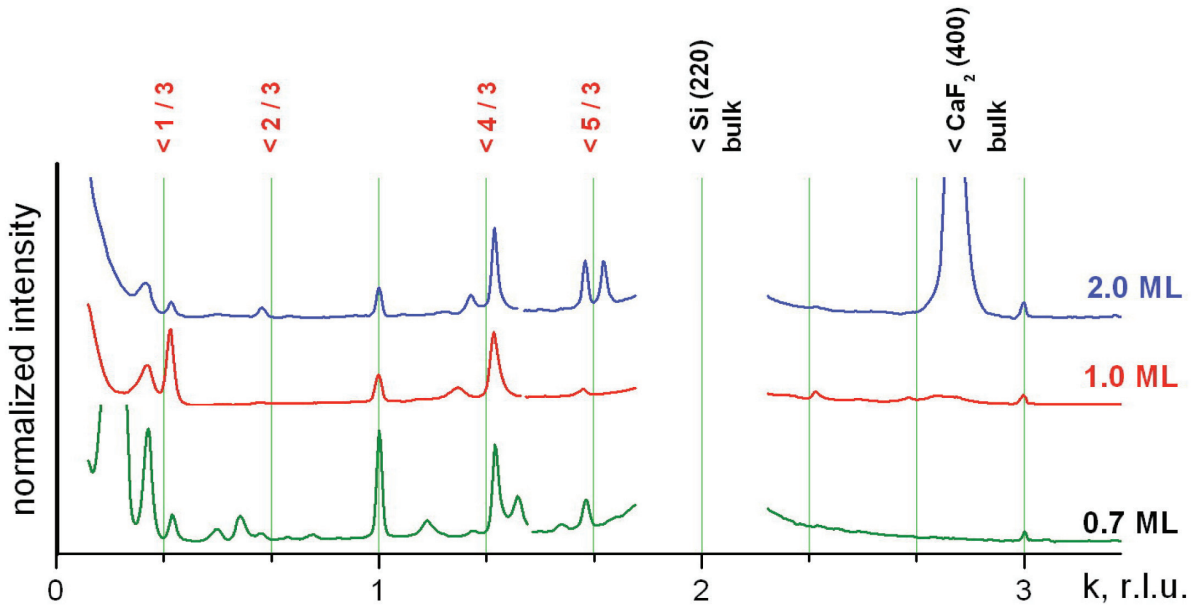

Fig. 4 Diffraction intensity profiles taken along K at H=0 for three different coverages.

another confirmation of the unusual CaF_2 (110)/Si (001) epitaxial relations.

To obtain information on geometry of the wetting layer along the surface normal, out-of-plane data was collected along the fractional order reciprocal lattice rods corresponding to the strongest in-plane reflections. At each point on the rod up to L=2.7 an ω-scan was measured in order to get the integrated intensity.

For both in-plane and out-of-plane measurements, attention has been paid to obtain data for symmetry equivalent reflections in order to minimize the systematic errors. Analysis of the collected structural data is underway.

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